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(54) POLYMER COMPOSITIONS

(71) We, MIDLAND SILICONES LIMITED, a British Company of Reading Bridge House, Reading, Berkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for effecting the cross-linking of organic polymers and to cross-linked organic polymers obtained thereby.

It is known to improve the properties of polyethylene and other inorganic polymers by heating the polymer in the presence of an organic peroxide as cross-linking agent. Such a process has the disadvantage however, that it requires careful control to avoid premature cross-linking of the polymer during processing, for example during extrusion. Care must also be exercised to ensure that articles prepared from the polymer retain their shape during subsequent heating to bring about the cross-linking process.

We have now found that by suitable treatment of the organic polymer in the presence of an organosilicon compound the organic polymer may be so modified that cross-linking may subsequently take place at temperatures significantly lower than those heretofore required.

In accordance with this invention there is provided a process for effecting cross-linking of an organic polymer which comprises (1) subjecting an organic polymer to mechanical working to induce the formation therein of free radical sites, said working being carried out in the presence of an organosilicon compound containing at least one silicon-bonded hydrolysable atom or radical and at least one silicon-bonded atom or radical reactive with the free radical sites

in the organic polymer, and (2) exposing the organic polymer to moisture.

The invention also includes a cross-linked organic polymer when prepared by the said process.

According to the initial step in the process of this invention the organic polymer is subjected to mechanical working to an extent sufficient to induce the formation of free radical sites in the polymer molecule. The formation of free radicals in organic polymers by mechano-chemical processes is now a well-known effect and is considered to involve the partial degradation of the polymer by chain scission. Various methods are known of mechanically working organic polymers to produce the free radical sites including milling, crushing, extruding, comminution, beating and high speed stirring. Any of these methods may be employed in the process of this invention. It is however preferred to generate the free radical sites by operations such as kneading or milling which involve intensive mastication and shearing of the polymer.

The degree of mechanical working of the organic polymer will depend on such factors as the type of polymer, its molecular weight and the number of free radical sites desired. The duration of the mechanical working operation will depend on the polymer itself and on the type of equipment employed. For example treatment in a rubber or plastic masticator or kneading apparatus is usually more expeditious than on a two-roll mill or mixer. Thus, depending on these variables, the generation of the desired free radical sites may involve working times varying from minutes to hours.

Mechanical working of the organic polymer may take place in the absence of externally applied thermal energy although it will be appreciated that some heat will nor-



mally be generated during the working process. In some cases however, depending on the nature of the polymer, additional heat may be required for example to render

5 the polymer more amenable to shear.

According to a further aspect of this invention the formation of free radical sites by mechanical means may be supplemented by the incorporation with the polymer of a
10 free radical generator such as an organic peroxide compound. When a peroxide or other temperature sensitive free radical generator is employed it will of course be necessary to ensure that the temperature
15 of the organic polymer is raised by self generated and/or externally applied heat to that at which the free radical generator is activated.

Any of the known free radical generating catalysts may be employed those preferred being organic peroxide compounds for example dicumyl peroxide, benzoyl peroxide, tertiary butylcumyl peroxide, lauroyl peroxide and azobis-isobutyronitrile. It will of course be understood that the presence
25 of an organic peroxide is best avoided in cases where this may lead to undesired degradation or modification of the polymer, for example the excessive liberation of hydrochloric acid from polyvinyl chloride which may be accelerated by the presence
30 of an organic peroxide.

Any organic polymer or copolymer which is susceptible to the mechanically induced
35 formation of free radical sites may be cross-linked according to the process of this invention. The method is however particularly applicable to the hydrocarbon and halogenated hydrocarbon polymers such as polyethylene, polypropylene, ethylene-propylene rubbers, polystyrene, polyvinyl
40 chloride, polytetrafluoroethylene, polyvinylidene chloride, polybutadiene copolymers and terpolymers of polybutadienes. Of particular interest in view of their widespread applications are polyethylene and polyvinyl chloride. The organic polymers may contain olefinically unsaturated sites in the
45 polymer chain, such as in polybutadiene, but the presence of such unsaturation is not essential. Although it is especially applicable to hydrocarbon and halogenated hydrocarbon polymers the process of this invention may also be employed to effect
50 cross-linking of other organic polymers for example, polysulphides, polyamides, polyesters, aminoplasts, epoxides and polyacrylates.

In accordance with the process of this invention mechanical working of the organic polymer to generate free radical sites is effected in the presence of an organosilicon compound, for example a silane or polysilane containing in the molecule at least
65 one silicon-bonded hydrolysable atom or

radical and at least one silicon-bonded atom or radical reactive with the free radical sites generated in the organic polymer.

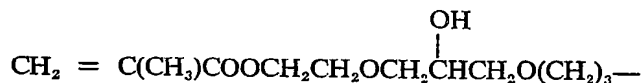
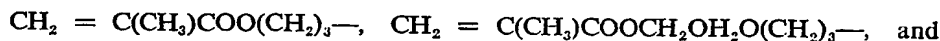
Examples of silicon-bonded hydrolysable groups which may be present in the organosilicon compound are halogen atoms, such as chlorine or bromine atoms, alkoxy radicals, particularly the more readily hydrolysable lower alkoxy radicals (i.e. those containing less than 6 carbon atoms) such as the methoxy, ethoxy and butoxy radicals, oximo radicals, acyloxy radicals such as acetoxy and propionoxy radicals and amino radicals linked to silicon through the hydrolytically unstable Si-N linkage. Preferred as the hydrolysable radicals are the alkoxy radicals as the hydrolysis of such radicals leads to the formation of more innocuous and less
70 corrosive by-products than does the hydrolysis of, for example, halogen atoms or acyloxy radicals.

The organosilicon compound should contain, in addition to the hydrolysable groups, a silicon-bonded atom or radical which is reactive with the free radical sites generated in the organic polymer. Preferred as the reactive moieties are the olefinically unsaturated hydrocarbon and hydrocarbonoxy radicals for example, vinyl, allyl, cyclohexenyl, bicycloheptenyl and gamma-methacryloxypropyl radicals.

Provided the specified hydrolysable and free radical-reactive substituents are present in the organosilicon compound the nature of any remaining substituents is not critical
90 except that they should not give rise to undesired side reactions. Thus the remaining valencies of the organosilicon compound may be satisfied with alkyl radicals, for example methyl, ethyl, propyl and octadecyl radicals, aryl radicals such as phenyl and naphthyl and substituted hydrocarbon radicals such as chlorophenyl or trifluoropropyl radicals.

Examples of operative organosilicon compounds therefore are methylvinyl dichlorosilane, methylvinyl dimethoxysilane, phenylvinyl dimethoxysilane, methylvinyl diacetoxysilane, vinyltriacetoxysilane, methylvinyl diacetoxime silane, allyltrimethoxysilane, sec-butyltrichlorosilane, vinylchlorodimethoxysilane, cyclohexenyltribromosilane, allyltributoxysilane and dimethylvinylacetoxysilane. Preferred as the organosilicon compounds for use in this invention are however the silanes containing three silicon-bonded hydrolysable group or atoms selected from halogen atoms, alkoxy radicals and acyloxy radicals and wherein the fourth valency of the silicon
125 atom is satisfied with a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, that is compounds of the general formula $R-Si-Y$, wherein R is a monovalent olefinically unsaturated hydro-
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carbon or hydrocarbonoxy radical, for example the vinyl, allyl, butenyl, cyclohexyl,



radicals and each Y is an alkoxy radical, for example the methoxy, ethoxy, propoxy or butoxy radical, a halogen atom, for example chlorine or bromine or an acyloxy radical for example the formyloxy, acetoxy or propionyloxy radicals. For the reasons previously stated herein the preferred silicon-bonded hydrolysable radicals are alkoxy radicals containing less than 6 carbon atoms. The preferred unsaturated silicon-bonded radicals are the vinyl and gamma-methacryloxypropyl radicals. In view of their commercial availability the most preferred organosilicon compounds are vinyltriethoxysilane and gamma-methacryloxypropyltrimethoxysilane.

The quantity of organosilicon compound is not critical and will in general, depend on the degree of cross-linking desired in the organic polymer. Up to 20 per cent by weight or more of the organosilicon compound, based on the weight of the organic polymer, may be used. Usually however from 0.5 to 5 per cent by weight will be sufficient.

If desired there can be present with the silane during mechanical working of the polymer a monomeric organic material such as methylmethacrylate, ethyl acrylate or maleic anhydride. The additional presence of such materials can be advantageous in some cases in as much as it can lead to an improvement in the degree of cross-linking of the organic polymer.

Following the mechanical working of the organic polymer in the presence of the organosilicon compound, the resulting product is then exposed to moisture to effect cross-linking of the polymer molecules. In such cases the moisture present in the atmosphere may be sufficient to permit the desired degree of cross-linking to take place. Generally however it is preferred to use an artificially moistened environment having a high Relative Humidity.

Preferably also the cross-linking reaction is expedited by incorporating with the polymer a silanol condensation catalyst. Such catalysts are well known in the art and include for example metal carboxylates such as dibutyltin dilaurate, stannous acetate, stannous octoate, lead naphthenate, zinc octoate, iron-2-ethyl-hexoate and cobalt naphthenate, organic metal compounds such as the titanium esters and chelates for example tetrabutyl titanate, tetranonyl titanate and bis(acetyl acetonyl)di-isopropyl titanate,

organic bases such as ethylamine, hexylamine, dibutylamine and piperidine and acids such as the mineral acids and organic fatty acids. The preferred catalysts are the alkyltin salts of carboxylic acids, for example dibutyltin dilaurate, dibutyltin dioctoate and dibutyltin diacetate.

When employed, the silanol condensation catalyst may be incorporated prior to during or following the mechanical working of the polymer. Most conveniently however, it is added during the working operation or generated *in situ* during the hydrolysis of for example, silicon-bonded chlorine atoms or acyloxy radicals if these are present in the organosilicon compound.

Although cross linking will take place at normal ambient temperatures, that is at about 25°C, the rate at which it takes place may be increased if desired by the application of heat.

If desired there may also be incorporated in the cross-linkable organic polymer polyfunctional silicon compounds which are known to function as cross-linking agents for siloxanes, for example tetraethyl orthosilicate, n-propyl orthosilicate, ethylpolysilicate, propyl polysilicate and butyl polysilicate.

By means of the process of this invention the cross-linking of organic polymers may be effected in a convenient manner. Thus for example, the organosilicon compound, and free-radical initiator if employed, may be added to the polymer together with the ingredients such as fillers, plasticisers, pigments and stabilisers which are normally incorporated just prior to the final processing operation. Following the addition of the silane to the polymer the desired mechanical degradation of the organic polymer may then be brought about during any one of more subsequent processing operations, for example during a mixing, extruding or moulding step. A more preferred method of operation however resides in performing the mechanical working of the organic polymer in the presence of the organosilicon compound at some time prior to the normal processing operations of, for example, mixing or extruding. Following the mechanical working operation the product may be stored in the form of a cross-linkable organic polymer until required for shaping and subsequent cross-linking by exposure to moisture. This invention therefore includes a cross-linkable organic polymer which has been

prepared by subjecting an organic polymer to mechanical working to induce the formation therein of free radical sites, said working being carried out in the presence of an organosilane containing at least one silicon-bonded hydrolysable atom or radical and at least one silicon-bonded atom or radical reactive with the free radical sites in the organic polymer.

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- If the cross-linkable organic polymer is to be stored for a significant period of time before use premature cross-linking of the polymer may be avoided by storage of the polymer under dry conditions and by delaying the incorporation of the siloxane condensation catalyst.

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- The following examples in which the parts are expressed as parts by weight illustrate the invention. The words Rigidex, Breon and Cycloc used in the examples are registered trade marks.

EXAMPLE 1

- 100 parts of polyethylene (Grade 9 Rigidex, without antioxidant) were placed in a Baker Perkins Type 3 masticator. Five parts of vinyltriethoxysilane were then added and the two components mixed together and masticated for 40 minutes. One part of dibutyltin diacetate was then added and the composition masticated for a further 5 minutes. The final product was then recovered and pressed into two sheets of 1/16 inch thickness.

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- The degree of cross-linking of the polyethylene was examined by measuring the proportion of polyethylene which had been rendered insoluble in xylene. In carrying out this test a portion (0.75 g.) of the polyethylene was refluxed in xylene (250 cc.) for 24 hours, thereafter recovering and weighing the portion which had not entered into solution. The weight of the insoluble portion was then expressed as a weight percentage of the original and the result designated the percentage insolubility.

- Of the two prepared sheets the percentage insolubility of one was measured for the sheet as prepared and a value of 20% obtained. The remaining sheet was stored for 2 months at 100% RH and 22°C. After this storage period the insolubility of the polyethylene was measured and a value of 40% obtained.

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- When the experiment was repeated employing an equal proportion of dibutyltin dilaurate in place of the dibutyltin diacetate values of 3% and 48% respectively were obtained for the insolubility of the polyethylene as treated and following 2 months storage at 100% RH and 22°C.

EXAMPLE 2

Employing the method of Example 1, 100 parts of polyethylene (Grade 9, Rigidex,

with antioxidant), 3 parts of vinyltriethoxysilane and 0.0375 parts of dicumyl peroxide were mixed and masticated for 10 minutes. One part of dibutyltin diacetate was then added and the composition masticated for a further 3 minutes.

The product was then pressed into two sheets of 1/16 inch thickness and the percentage insolubility of the polyethylene measured on one sheet as prepared. A value of 49% was obtained. The second sheet was stored for 2 weeks at 100% RH and 22°C and then placed in a steam autoclave at 100°C for 3 hours. Measurement of percentage insolubility of the product gave a value of 62.

EXAMPLE 3

The experiment described in Example 2 was repeated except that the dicumyl peroxide was replaced with 0.033 parts of benzoyl peroxide and 0.5 part of tetraethylorthosilicate was added as a mixture with the dibutyltin diacetate.

In this case the percentage insolubility of the product as prepared (measured on the unshaped product) was zero, that is, the same as that for untreated polyethylene. However, after storage of the product (in the form of 1/16 inch sheet) for 10 days at 100% RH and 22°C the percentage insolubility had risen to 41%.

EXAMPLE 4

The experiment described in Example 2 was repeated except that 0.02 parts of dibutyltin diacetate and 2 parts of $\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$ were employed and all of the ingredients were mixed together prior to the mastication step. The product (unshaped) had zero percentage insolubility as prepared but a percentage insolubility of 46 after storage in sheet form (1/16 inch thick) for 7 days at 100% RH and 22°C, followed by 2 hours in a steam autoclave at 100°C.

EXAMPLE 5

95 parts of Grade 9 Rigidex polyethylene containing antioxidant, 5 parts of Grade 9 Rigidex polyethylene not containing antioxidant, 2 parts of vinyltriethoxysilane, 0.04 parts of dicumyl peroxide were mixed and masticated in a Buss Ko-Kneader (Type PR 6) for 2 minutes to give mix A. A second mix (B) was then prepared by mixing in the kneader 100 parts of Grade 9 Rigidex polyethylene and 2 parts of dibutyltin dilaurate and the mix masticated for about 2 minutes. 90 parts of Mix A and 10 parts of Mix B were then fluxed together on a 2 roll mill and a 1/16 inch thick sheet prepared from the product.

When tested for percentage insolubility according to the method described in Ex-

ample 1 the sheet as prepared gave a value of zero. After ageing the sheet for 18 hours in a steam autoclave at 100°C the percentage insolubility of the polyethylene was 51.

5 EXAMPLE 6

100 parts of a polyacrylate [Acryloid K-120 N] and 20 parts of gamma-methacryloxypropyltrimethoxysilane were mixed and masticated in a Baker Perkins Type 3 Masticator for 20 minutes. The product obtained was granulated, 50 g. of the granules mixed with 1.0 cc of dibutyltin acetate and the product hot pressed into a sheet 1/16 inch thick.

15 The percentage insolubility of the product was measured by subjecting a 1 g. sample to immersion in 30 cc of benzene for 24 hours. When subjected to this test the percentage insolubility of the product as prepared was zero. After one day in a steam autoclave at 100°C the percentage insolubility had risen to 26.

EXAMPLE 7

100 parts of polyvinyl chloride (Breon 115), 4.6 parts of gamma-methacryloxypropyltrimethoxysilane and 41.5 parts of methyl methacrylate were mixed and masticated in a Baker Perkins Type 3 masticator under cooling for 15 minutes. The product was then granulated, 50 g. of the granules mixed with 1.5cc of dibutyltin diacetate and the product hot pressed into a sheet 1/16 inch thick.

35 Percentage insolubility of the product was measured by immersing a 1 g. sample in 30 cc of tetrahydrofuran for 24 hours and recovering the insoluble portion. After storage for 9 days at 100% RH and 22°C the product had a percentage insolubility of 30 according to this test. When this storage period was supplemented by 1 day at 100% RH and 70°C the percentage insolubility of the product had increased to 40.

45 EXAMPLE 8

100 parts of acrylonitrile-butadienestyrene copolymer [Cycolac ABS polymer Type H granules], 10 parts of gamma-methacryloxypropyltrimethoxysilane and 10 parts of methyl methacrylate were mixed and masticated under cooling in a Baker Perkins Type 3 mastication for 13 minutes, the product thereafter being granulated.

50 50 g. of the granulated product were mixed with 1.5 cc. of dibutyltin diacetate and the mixture hot pressed into a 1/16 inch thick sheet.

60 Percentage insolubility of the product was measured by immersing a 1 g. sample of the sheeted product in 30 cc. of methyl-ethyl ketone at room temperature for 24 hours.

When the sheet was stored for 3 days at 100% RH and 22°C an insolubility value of 38% was obtained. When this storage was supplemented by 24 hours at 100% RH and 70°C the insolubility value increased to 47%. 65

WHAT WE CLAIM IS:—

1. A process for effecting cross-linking of an organic polymer which comprises (1) 70
subjecting an organic polymer to mechanical working to induce the formation therein of free radical sites, said working being carried out in the presence of an organosilicon compound containing at least one silicon-bonded hydrolysable atom or radical and at least one silicon-bonded atom or radical reactive with the free radical sites in the organic polymer, and (2) exposing the organic polymer to moisture. 75

2. A process as claimed in Claim 1 wherein the organic polymer is a hydrocarbon or halogenated hydrocarbon.

3. A process as claimed in Claim 2 wherein the organic polymer is polyvinyl chloride. 85

4. A process as claimed in Claim 2 wherein the organic polymer is polyethylene.

5. A process as claimed in any of Claims 1 to 4 wherein the organosilicon compound has the general formula $RSiY_3$ wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical and each Y represents the halogen atom, an alkoxy radical or an acyloxy radical. 90

6. A process as claimed in Claim 5 wherein each Y represents an alkoxy radical containing less than 6 carbon atoms. 100

7. A process as claimed in Claim 5 or Claim 6 wherein R represents the vinyl radical or the gamma-methacryloxypropyl radical.

8. A process as claimed in Claims 5—7 wherein the organosilicon compound is vinyltriethoxysilane or gamma-methacryloxypropyltrimethoxysilane. 105

9. A process as claimed in any one of the preceding claims wherein the organosilicon compound is employed in a proportion of from 0.5 to 5 per cent based on the weight of the organic polymer. 110

10. A process as claimed in any one of the preceding claims wherein there is also present during the mechanical working of the polymer a free radical generating catalyst. 115

11. A process as claimed in Claim 10 wherein the free radical generating catalyst is an organic peroxide compound. 120

12. A process as claimed in any one of the preceding claims wherein the silanol condensation catalyst is incorporated in the organic polymer prior to, during or following the mechanical working step or is gener- 125

ated in situ during the hydrolysis of the organosilicon compound.

13. A process as claimed in Claim 12 wherein the silanol condensation catalyst is an organic tin compound.

14. A process as claimed in Claim 13 wherein the organic tin compound is an alkyltin salt of a carboxylic acid.

15. A process as claimed in Claim 14 wherein the organic tin compound is selected from dibutyltin dilaurate, dibutyltin dioctate or dibutyltin diacetate.

16. A process for effecting the cross-linking of an organic polymer substantially as described with reference to the Examples.

17. A cross-linked organic polymer whenever prepared by the process claimed in any one of the preceding claims.

18. A cross-linkable organic polymer which has been prepared by subjecting an organic polymer to mechanical working to induce the formation therein of free radical sites, said working being carried out in the presence of an organosilicon compound con-

taining at least one silicon-bonded hydrolysable atom or radical and at least one silicon-bonded atom or radical reactive with the free radical sites in the organic polymer.

19. A cross-linkable organic polymer as claimed in Claim 18 wherein the organosilicon compound is selected from vinyltriethoxysilane and gamma-methacryloxypropyltrimethoxysilane.

20. A cross-linkable organic polymer as claimed in Claim 18 or Claim 19 which also contains a silanol condensation catalyst.

20. A cross-linkable organic polymer as claimed in Claim 20 wherein the silanol condensation catalyst is an alkyltin salt of a carboxylic acid.

22. A cross-linkable organic polymer as claimed in any one of Claims 18—21 wherein there is also present an organosilicon cross-linking agent.

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